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(19) (CA) **CANADIAN PATENT** (12)

(54) THERMOPLASTIC POLYCARBONATE MOLDING MATERIALS WITH
IMPROVED MOLD RELEASE

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THERMOPLASTIC POLYCARBONATE MOLDING MATERIALS
WITH IMPROVED MOLD RELEASE

Abstract of the Disclosure

The present invention is concerned with thermoplastic molding materials of high molecular weight, thermoplastic, aromatic polycarbonates based on aromatic dihydroxy compounds and containing from about 0.01 to 0.1% by weight of esters of saturated aliphatic carboxylic acids with 10 to 20 C atoms and 4-hydric to 6-hydric alcohols.

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THERMOPLASTIC POLYCARBONATE MOLDING MATERIALS
WITH IMPROVED MOLD RELEASE

Background of the Invention

5 The invention relates to thermoplastic molding materials of high molecular weight, thermoplastic, aromatic polycarbonates based on aromatic dihydroxy compounds.

10 High molecular weight, thermoplastic, aromatic polycarbonates are employed in numerous technical fields of application, because of their typical tough and elastic properties. A disadvantage is their poor mold release when injection-molded, which frequently results in relatively long cycle times. However, for economic and technical reasons, it is desirable to shorten the cycle times as far as possible so as to manufacture larger numbers of moldings per unit time on the injection molding machines. This can be achieved by mold release at higher temperatures. The objective is, therefore, to so modify the polycarbonate melt that the release of the molding from the wall of the mold takes place with low release forces and at high temperatures, without sticking of the solidified melt to the wall of the mold. Easy mold release at high temperatures is in particular also desired in the case of complicated moldings which are molded in molds with parts which cannot be cooled (for example, cross-webs, cores and the like). Undesired sticking of the moldings and damage of the molds on releasing the moldings (breakage of pins and the like), coupled with great losses of time, are frequently the consequence.

In the past, long-chain aliphatic carboxylic acid esters of monohydric and trihydric alcohols have been added
LeA 16,284

to improve the mold release of aromatic polycarbonates, in accordance with Canadian Patents 918,838 and 980,037 and U.S. Patents 3,784,595 and 3,836,499. However, a disadvantage of these mold release agents is the

5 deterioration in mechanical properties on prolonged heat exposure, as a result of which the aromatic polycarbonates which have been modified according to Canadian Patents 918,838 and 980,037 and U.S. Patents 3,784,595 and 3,836,499, so as to give easy mold release no longer satisfy certain technical requirements. A further disadvantage

10 is the ready volatility of the fatty acid esters of glycerol, which particularly manifests itself as a disadvantage at the high temperatures at which polycarbonate is processed.

15 Summary of the Invention

By means of the present invention, it is possible to provide high molecular weight, thermoplastic, aromatic polycarbonates which show a mold release behavior which is adequate for all technical applications and

20 also show a level of mechanical properties which is, even after prolonged heat exposure, comparable to the corresponding aromatic polycarbonates which do not contain mold release agents. The mold release behavior at higher mold temperatures, whereby the advantages described

25 above are achieved, is particularly desirable.

According to the present invention, there are provided thermoplastic molding materials comprising thermoplastic, aromatic polycarbonates having molecular weights, \bar{M}_w , from about 10,000 to 200,000 based on

30 aromatic dihydroxy compounds and containing from about 0.01-

0.1, preferably from about 0.05 - 0.1, % by weight of an ester of saturated aliphatic carboxylic acids with 10 to 20 C atoms and aliphatic 4-hydric to 6-hydric alcohols.

The instant invention also relates to articles
5 molded from the thermoplastic materials described above.

Detailed Description of the Invention

Alcohols having 4 OH groups are those having preferably between 4 and 16 carbon atoms, most preferably between 4 and 8 carbon atoms; alcohols having 5 OH groups
10 are those having preferably between 5 and 18 carbon atoms, most preferably between 5 and 10 carbon atoms; alcohols having 6 OH groups are those having preferably between 6 and 18 carbon atoms, most preferably between 6 and 12 carbon atoms.

15 Esters of saturated aliphatic C_{10} - C_{20} -carboxylic acids and aliphatic alcohols with 4 to 6 OH groups are, according to the invention, those which result from the complete esterification of the 4 to 6 OH groups of the alcohols with one, or more than one, of the C_{10} - C_{20} -
20 carboxylic acids in question.

The surprising aspect of the invention is that in contrast to the known processes only small amounts of carboxylic acid esters (<0.1%) are required to achieve adequate mold release for all fields of application.

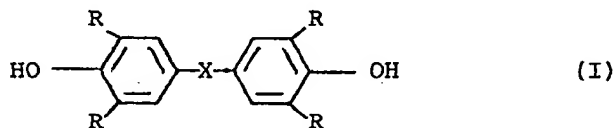
25 The polycarbonate molding materials according to the invention are distinguished by outstanding ease of mold release, a particular advantage being that the mold release can be effected within a very broad temperature range. As a result, the injection cycles become
30 independent of temperature fluctuations in the injection mold, which is a great advantage for the plastics processor.

The mechanical properties and the long-term use properties of the polycarbonates which have been modified

according to the present invention so as to give easy mold release are identical with those of the pure polycarbonates. No deterioration of the mechanical properties and no molecular weight degradation is observed even as a result of prolonged heat exposure (130°C for 300 hours).

Aromatic polycarbonates in the sense of the present invention are to be understood as homopolycarbonates and copolycarbonates which are based, for example, on one or more of the following bisphenols: hydroquinone, resorcinol, dihydroxydiphenyls, bis-(hydroxyphenyl)-alkanes, bis-(hydroxyphenyl)-cycloalkanes, bis-(hydroxyphenyl)-sulphides, bis-(hydroxyphenyl)-ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulphoxides, bis-(hydroxyphenyl)-sulphones and α,α -bis-(hydroxyphenyl)-diisopropyl-benzenes, as well as their nuclear-alkylated and nuclear-halogenated compounds. These and further suitable aromatic dihydroxy compounds are described, for example, in U. S. Patents 3,028,365; 2,999,835; 3,148,172; 3,271,368; 2,991,273; 3,271,367; 3,280,078; 3,014,891 and 2,999,846; in Canadian Patents 846,265; 973,993; 1,000,895 and 578,885; and in the monograph "H. Schnell, Chemistry and Physics of Polycarbonates, Interscience Publishers, New York, 1964".

Preferred bisphenols are those of the formula I

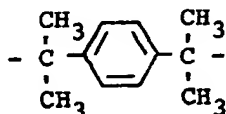


in which

R is identical or different and denotes H, C₁-C₄-alkyl, Cl or Br

and in which

5 X is a bond, C₁-C₈-alkylene, C₂-C₈-alkylidene, C₅-C₁₅-cycloalkylene, C₅-C₁₅-cycloalkylidene, -SO₂- or



10 Examples of these bisphenols are 4,4'-dihydroxydiphenyl, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, α,α'-bis-(4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-
 15 chloro-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulphone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(3,5-dimethyl-4-hydroxyphenyl)-cyclohexane, α,α'-bis-(3,5-
 20 dimethyl-4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane and 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane.

Examples of particularly preferred bisphenols are 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-
 25 hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

Preferred aromatic polycarbonates are those based
 30 on one or more of the bisphenols mentioned as being preferred.
Le A 16 284

Particularly preferred copolycarbonates are those based on 2,2-bis-(4-hydroxyphenyl)-propane and optionally, one of the other bisphenols mentioned as being particularly preferred. Further particularly preferred polycarbonates are those based
 5 solely on 2,2-bis-(4-hydroxyphenyl)-propane or 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane.

The aromatic polycarbonates can be manufactured according to known processes, e.g. in accordance with the melt trans-esterification process from bisphenols and diphenyl
 10 carbonate, and in accordance with the two-phase boundary process from bisphenols and phosgene, as described in the above-mentioned literature.

The aromatic polycarbonates can also be branched as a result of the incorporation of small amounts of polyhydroxy
 15 compounds, e.g. from about 0.05 - 2.0 mol % based on the bisphenols employed. Polycarbonates of this nature are described, for example, in Canadian Patents 820,415; 986,128 and 1,016,294; British Patent 1,079,821 and U. S. Patent 3,544,514. Some examples of the polyhydroxy compounds which can be used are
 20 phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptene-2, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptane, 1,3,5-tri-(4-hydroxyphenyl)-benzene, 1,1,1-tri-(4-hydroxyphenyl)-ethane, tri-(4-hydroxyphenyl)-phenylmethane, 2,2-bis-[4,4-(4,4'-dihydroxydiphenyl)-cyclohexyl]-propane, 2,4-bis-(4-hydroxyphenyl)-
 25 isopropyl-phenol, 2,6-bis-(2'-hydroxy-5'-methylbenzyl)-4-methyl-phenol, 2,4-dihydroxybenzoic acid, 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane and 1,4-bis-(4',4"-dihydroxytriphenylmethyl)-benzene.

The aromatic polycarbonates should as a rule have molecular weights M_w of about 10,000 to more than 200,000, preferably of about 20,000 to 80,000.

5 The esters which are effective according to the present invention are reaction products of 4-hydric to 6-hydric alcohols such as, for example, erythritol, arabitol, adonitol, mannitol and dulcitol, and especially meso-erythritol, xylitol, sorbitol and pentaerythritol, with saturated aliphatic carboxylic acids with 10 to 20 C atoms.

10 All aliphatic saturated monocarboxylic acids between capric acid and eicosanoic acid are suitable, optionally together with polycarboxylic acids with 10 to 20 C atoms, for example, capric acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric

15 acid, stearic acid, monodecanoic acid, eicosanoic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, brassylic acid and thapsic acid.

Suitable carboxylic acids with 10 to 20 C atoms are in particular myristic acid, palmitic acid and stearic acid.

20 The alcohols can be esterified with either one or several of these carboxylic acids.

Examples of esters to be used according to the invention are pentaerythritol tetrastearate, pentaerythritol tetrapalmitate, pentaerythritol tetramyristate, pentaerythritol tetralaurate, mesoerythritol tetralaurate, mesoerythritol tetrastearate, mesoerythritol tetramargaric acid ester, mesoerythritol tetramyristate, mesoerythritol tetracosate, xylitol pentastearate, xylitol pentatridecanoic acid ester, xylitol pentapalmitate, arabitol pentastearate,

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Le A 16 284

arabitol pentapalmitate, sorbitol hexastearate, sorbitol hexapentadecanoic acid ester, sorbitol hexapalmitate, dulcitol hexamondecanoic acid ester, dulcitol hexapalmitate, mannitol hexastearate, mannitol hexamyrystate and mannitol hexalaurate.

Single esters of stearic acid and palmitic acid are used preferentially. If the monocarboxylic acids are partially replaced by polycarboxylic acids, higher-molecular carboxylic acid esters are obtained, which are also outstandingly suitable for the mold release of polycarbonates. Equally, mixtures of the esters according to the invention of saturated aliphatic C_{10} - C_{20} -carboxylic acids and alkanols containing 4 to 6 OH groups are suitable.

The carboxylic acid esters to be used according to the invention are prepared according to customary processes, for example, in accordance with the Einhorn process using pyridine as the acid-binding agent, from alcohol and acid chloride in an inert solvent, or in the melt from the alcohol and acid with or without esterification catalysts such as, for example, p-toluenesulphonic acid. The esterification is carried out at 200 - 250°C. Such processes are described, for example, in "Houben-Weyl, Methoden der organischen Chemie (Methods of Organic Chemistry), Georg Thieme Verlag, Stuttgart, 1952, 4th Edition, Volume VIII, page 516 et seq.

The incorporation of the carboxylic acid esters to be used according to the invention into the high molecular weight, thermoplastic polycarbonates is effected, for example, by applying the substances, which are normally in the form of a powder, onto the granules of the polycarbonate by tumbling and subsequently extruding the material on a twin-screw

extruder at 280°C to form a ribbon, which is granulated. However, the mold release agent can also be incorporated during manufacture of the solid polycarbonate. In that case the ester is either admixed, as a solution in a solvent, with
5 the polycarbonate solution before reaching the devolatilization screw, or is metered, without solvent, into the polycarbonate melt.

The addition of the esters to be used according to the invention has no adverse effect on either the transparency
10 or the color of the polycarbonate. Optionally, dyestuffs, pigments, stabilizers, flameproofing agents or fillers such as glass fibers can also be added to the polycarbonate without thereby impairing the effectiveness of the mold release agent.

15 The thermoplastic polycarbonate molding materials according to the invention are used wherever moldings are manufactured fully automatically, in large numbers and with short cycle times, by the injection molding process. This applies, for example, to the use in the electrical industry
20 and the optical field, for example, for terminal bars, bobbins, complicated housings such as projector housings, floors of switch cabinets and the like, and for particularly complicated moldings which are molded in molds in which there are zones which differ greatly in temperature. When manufacturing
25 such articles, no mold release difficulties are found even at elevated temperatures.

The effectiveness of the esters to be used according to the invention is measured in terms of the mold release forces required for the mold release of injection-molding

materials. In the examples which follow, these forces are measured by rendering visible, via an optical and at the same time recording indicator instrument, the pressure which builds up in the hydraulic cylinder of the ejector system during mold release.

The examples which follow are intended to explain the subject of the invention in more detail:

EXAMPLES

I. The aromatic polycarbonates used.

General instructions for the preparation of polycarbonates.

Approx. 454 parts of 4,4'-dihydroxydiphenyl-2,2-propane and 9.5 parts of p-tert.-butylphenol are suspended in 1.5 liter of water. The oxygen is removed from the reaction mixture in a 3-necked flask equipped with a stirrer and gas inlet tube, by passing nitrogen through the reaction mixture for 15 minutes while stirring. 355 parts of 45% strength sodium hydroxide solution and 1,000 parts of methylene chloride are then added. The mixture is cooled to 25°C. While maintaining this temperature by cooling, 237 parts by phosgene are added over a period of 120 minutes. An additional amount of 75 parts of a 45% strength sodium hydroxide solution is added after 15-30 minutes or after the absorption of phosgene has started. 1.6 parts of triethylamine are added to the resulting solution and the mixture is stirred for a further 15 minutes. A highly viscous solution is obtained, the viscosity of which is regulated by adding methylene chloride. The aqueous phase is separated off. The organic phase is washed with water until free from salt

and alkali. The polycarbonate is isolated from the washed solution and dried. The polycarbonate has a relative viscosity of 1.29 - 1.30, measured in a 0.5% strength solution of methylene chloride at 20°C. This corresponds approximately to a molecular weight of 32,000. The polycarbonate thus obtained is extruded and granulated.

A.) An aromatic polycarbonate based on 4,4'-dihydroxydiphenylpropane-2,2 (bisphenol A) of relative viscosity $\eta_{rel} = 1.30$, $M_{LS} = 28,000$ (M_{LS} = molecular weight determined by light scattering).

The viscosities are measured at 25°C in methylene chloride, at a concentration of 5 g/l.

B.) An aromatic polycarbonate based on 90 mol % of bisphenol A and 10 mol % of 4,4'-dihydroxy-3,3',5,5'-tetrabromodiphenylpropane-2,2 (tetrabromobisphenol A) of relative viscosity $\eta_{rel} = 1.33$, $M_{LS} = 37,000$.

C.) An aromatic polycarbonate based on 70 mol % of bisphenol A and 30 mol % of 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylpropane-2,2 (tetramethylbisphenol A) of relative viscosity $\eta_{rel} = 1.28$, $M_{LS} = 30,000$.

II. The carboxylic acid esters used.

D.) Pentaerythritol tetrastearate, melting point 76°C.

E.) Pentaerythritol tetrapalmitate, melting point 68°C.

F.) Xylitol pentastearate, melting point 66°C.

G.) Sorbitol hexapalmitate, melting point 69°C.

H.) (Comparison example). Triglyceride with acid radicals

of palmitic acid, stearic acid and myristic acid in the ratio of 1 : 1 : 0.1, melting point 48°C. (Compare Canadian Patent 918,388 and U. S. Patent 3,784,595).

5 The mold release behavior of the polycarbonates of Examples 1 - 9 is tested on a conical cylinder of 35 mm length and of 40 and 42 mm diameter, and 2 mm wall thickness, by measuring the pressure which builds up in the ejector system. The mold release pressures and temperatures are indicated in Table 1.

10 Moldings injection-molded from the polycarbonates of Examples 1 - 9 at 270°C have the properties described in Table 2.

Examples 1, 4 and 6 correspond to polycarbonates A, B and C, respectively, without mold release agent.

15 Example 2

0.1 kg of mold release agent D is applied to 99.9 kg of polycarbonate A by tumbling in a drum at room temperature and the material is then extruded to a ribbon on an extruder at 280°C, and is granulated. The mold release behavior is
20 tested as in Example 1. The properties are described in Tables 1 and 2.

Example 3

0.01 kg of mold release agent D is applied to 99.99 kg of polycarbonate A by tumbling in a drum at room temperature and
25 the material is then extruded to a ribbon on an extruder at 280°C, and is granulated. The mold release

behavior is tested as described in Example 1. The properties are described in Tables 1 and 2.

Example 5

5 0.1 kg of mold release agent E is applied to 99.9 kg of polycarbonate B by tumbling in a drum at room temperature and the material is then extruded to a ribbon on an extruder at 310°C, and is granulated. The mold release behavior is tested as in Example 1. The properties are described in Tables 1 and 2.

10 Example 7

15 0.1 kg of mold release agent F is applied to 99.9 kg of polycarbonate C by tumbling in a drum at room temperature and the material is then extruded to a ribbon on an extruder at 300°C, and is granulated. The mold release behavior is tested as in Example 1. The properties are described in Tables 1 and 2.

Example 8

20 0.1 kg of mold release agent G is applied to 99.9 kg of polycarbonate A by tumbling in a drum at room temperature and the material is then extruded to a ribbon on an extruder at 280°C, and is granulated. The mold release behavior is tested as in Example 1. The properties are described in Tables 1 and 2.

Example 9 (Comparison Example)

25 0.5 kg of mold release agent H is applied to 99.5 kg of polycarbonate A by tumbling in a drum at room tempera-

1109174

ture and the material is then extruded to a ribbon on an extruder at 280°C, and is granulated. The mold release behavior is tested as in Example 1. The properties are described in Tables 1 and 2.

TABLE 1

Mold release behavior of the various polycarbonates

Example	Composition	mold release pressure	Mold release temperature, °C		
			150°C	160°C	170°C
1	100% PC A	"	40 bar	30 bar	85 bar
2	99.9% PC A 0.1% mold release agent D	"	20 "	10 "	5 "
3	99.99% PC A 0.01% mold release agent D	"	25 "	20 "	40 "
4	100% PC B	"	44 "	36 "	80 "
5	99.9% PC B 0.1% mold release agent E	"	20 "	10 "	20 "
6	100% PC C	"	48 "	35 "	82 "
7	99.9% PC C 0.1% mold release agent F	"	15 "	10 "	8 "
8	99.9% PC A 0.1% mold release agent G	"	18 "	8 "	6 "
9	99.5% PC A 0.5% mold release agent H	"	40 "	15 "	37 "

TABLE 2

Moldings injection-molded from the polycarbonates of Examples 1 - 9 at 270°C have the following properties:

Dimension		1	2	3	4	5	6	7	8	9
η_{rel}	%	1.30	1.29	1.29	1.33	1.32	1.28	1.27	1.29	1.28
elongation at break	%	53,455	120	110	100	105	125	120	115	110
notched impact strength	KJ/m ³	53,453	44	43	38	40	46	45	42	36
Vicat B	°C	53,460	150	150	155	153	156	155	150	145
elongation at break *)	%	53,455	115	100	100	95	120	105	110	60
after heat treatment										
Vicat B	°C	53,460	150	148	150	153	154	153	148	135
after heat treatment *)										

*) the heat treatment was carried out for 300 hours at 130°C in air.

1109174

It is to be understood that any of the components and conditions mentioned as suitable herein can be substituted for its counterpart in the foregoing examples and that although the invention has been described in considerable detail in the
5 foregoing, such detail is solely for the purpose of illustration. Variations can be made in the invention by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

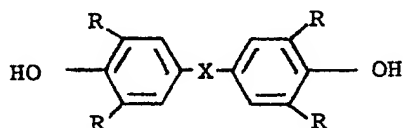
The embodiments of the invention in which exclusive property or privilege is claimed are defined as follows:

1. Thermoplastic molding materials comprising thermoplastic, aromatic polycarbonates having molecular weights, \bar{M}_w , from about 10,000 to 200,000 based on aromatic dihydroxy compounds and containing from about 0.01 to 0.1% by weight of esters of saturated aliphatic carboxylic acids with 10 to 20 C atoms and aliphatic 4-hydric to 6-hydric alcohols.

2. Thermoplastic molding materials according to Claim 1 containing from about 0.05 to 0.1% of the esters.

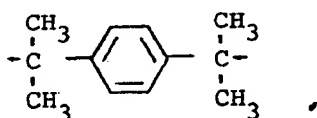
3. Thermoplastic molding materials according to Claim 1 wherein the esters are of 4-hydric alcohols having between 4 and 16 carbon atoms or of 5-hydric alcohols having between 5 and 18 carbon atoms or of 6-hydric alcohols having between 6 and 18 carbon atoms.

4. Thermoplastic molding materials according to Claim 1 wherein the aromatic dihydroxy compounds are those of the general formula (I)



wherein R is identical or different and denotes H, $\text{C}_1\text{-C}_4$ -alkyl, Cl or Br and

wherein X is a bond, $\text{C}_1\text{-C}_8$ -alkylene, $\text{C}_2\text{-C}_8$ -alkylidene, $\text{C}_5\text{-C}_{15}$ -cycloalkylene, $\text{C}_5\text{-C}_{15}$ -cycloalkylidene, $-\text{SO}_2-$ or



5. Thermoplastic molding compositions according to Claim 1 wherein the aromatic polycarbonates include from about 0.05 to 2 mol % by weight, based on the aromatic dihydroxy compounds employed, of polyhydroxy compounds.

6. Thermoplastic molding compositions according to Claim 1 wherein the molecular weights of the polycarbonates are from about 20,000 to 80,000.

7. Thermoplastic molding compositions according to Claim 1 wherein the saturated aliphatic carboxylic acids are myristic acid, palmitic acid and stearic acid.

8. Thermoplastic molding compositions according to Claim 1 containing dyestuffs, pigments, stabilizers, flame proofing agents or fillers.

9. Articles molded from the thermoplastic molding compositions of Claim 1.

10. In the process for molding thermoplastic polycarbonates, the improvement which comprises adding to the thermoplastic, aromatic polycarbonates having molecular weights, \bar{M}_w , from about 10,000 to 200,000 based on aromatic dihydroxy compounds from about 0.01 to 0.1 % by weight of a mold release agent selected from the group consisting of the esters of saturated aliphatic carboxylic acids with 10 to 20 C atoms and aliphatic 4-hydric to 6-hydric alcohols.

11. In the process of Claim 10 the esters are of 4-hydric alcohols having between 4 and 16 carbon atoms or of 5-hydric alcohols having between 5 and 18 carbon atoms or of 6-hydric alcohols having between 6 and 18 carbon atoms.

